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A supercritical oxidation system for the determination of carbon isotope ratios in marine dissolved organic carbon

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Abstract

An analytical oxidation system employing supercritical oxidation has been developed. It is designed to measure the concentration and the natural carbon isotope ratios (^{13}C, ^{14}C) of dissolved organic carbon (DOC) and is especially suited for marine samples. The oxidation takes place in a ceramic tube at 650°C and 350 bar, bringing the seawater in the supercritical state. Oxygen is used as oxidant and copper as a catalyst to ensure a complete oxidation. The system is tested by oxidizing urea, phthalic acid, tannic acid and other materials. The precisions are estimated to be 1‰ in ^{13}C abundance, 2% in ^{14}C abundance and 3% in DOC concentration. The blank is 9 μM of carbon and has a ^{14}C content of 80 pmC, measured by oxidizing traces of natural and synthetic material in distilled water. The ^{14}C is measured by accelerator mass spectrometry, the ^{13}C isotope ratio by isotope ratio mass spectrometry. This is, to our knowledge, the first analytical application of supercritical oxidation.

1. Introduction

Water at a pressure and temperature above 220 bar and 374°C is in the supercritical state. This is an attractive reaction regime for many applications because of the high mixing and reaction rates. Oxidation in the supercritical state is suitable for the combustion of organic material dissolved or suspended in water [1]. It has been developed for the destruction of waste streams that cannot be treated with biological methods. Even very stable compounds such as chlorophenol, *o*-cresol, pyridine and trichloroethene are completely oxidized. Typical conditions in these industrial processes are temperatures from 300°C to 500°C and residence times of 1–20 min.

As far as we know, no analytical applications of supercritical oxidation have been published so far. Yet the continuous nature, the robustness of the oxidation against interfering compounds and the aggressive oxidizing conditions make it a very reliable oxidation technique. Here we employ it for the measurement of isotope ratios in dissolved organic carbon (DOC), especially in marine samples. In that application, we use a further advantage of the supercritical state, namely that the salt remains dissolved. Other possible analytical applications of supercritical oxidation include the removal of interfering organic matrices (e.g., humic acids in cathodic stripping voltammetry [2]) and a continuous DOC analyzer.

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The measurement of marine DOC isotopic ratios is of great importance for the study of the global carbon cycle. An important issue is the role of marine biota in that cycle. The removal of carbon and nutrients from the surface of the ocean as organic material, particulate or dissolved in the water, has a large influence on the atmospheric CO_2 concentrations [3]. The natural carbon isotope ratios of DOC (and other carbon pools) render information on the nature and velocity of these processes [4].

The ratio of ^{13}C to ^{12}C varies between carbon compounds from different origins. This allows for the determination of the source of carbon containing compounds when they cannot be distinguished by chemical analysis . For example methane derived from bacterial processes contains around 4% less ^{13}C than methane from natural gas. In the marine environment the goal is to distinguish between organic matter formed in the marine environment itself and organic matter entrained by rivers.

The abundance of ^{14}C reflects the time that has passed since the carbon containing matter was part of a living organism (and thus in isotopic equilibrium with the atmosphere). This time is usually referred to as its ''age''. Its application in archaeology is best known, but it is also of great importance in carbon cycle research. As it is often impossible to measure fluxes to and from carbon reservoirs such as DOC directly, they have to be calculated from the age of the carbon in that reservoir.

Measuring the concentration of dissolved organic carbon in seawater is problematic, and several methods have been developed. The problems are caused by the very low concentrations (typically 40 μM) and the chemical stability of the DOC that hinders the oxidation. Two factors are crucial in all methods: (1) a blank that is as low, constant and as accurately known as possible and (2) a complete oxidation of even the most stable chemicals. The central step in measuring concentration or isotopic ratios of DOC is its oxidation to CO_2 . For this step four methods are known in the literature. Most of the reports concern only small water samples (5 ml) enough only for concentration measurements. For isotope analysis larger samples (500 ml) are needed.

The oldest method is wet chemical oxidation (WCO) with $K_2S_2O_8$ at 130°C [5,6]. This method offers reliable results for small samples (5 ml) [7]. The persulfate does not only oxidize the DOC, but also the chloride that is present in a much higher concentration. The chlorine formed in this way causes difficulties in the upscaling by the factor of 100 needed for accurate ^{14}C measurements. The best reported blank is 19 μM C [5].

An alternative is the dry combustion method. This involves (freeze) drying of the sample followed by sealed tube oxidation with CuO. Oxidation is complete, but extremely careful procedures are required to prevent contamination [8,9]. Another problem is either the loss of material during the drying process or the incomplete removal of water that leads to breakage of the tubes during combustion. The blank reported is <10 μM C [7].

Most commonly used is the high temperature catalytic oxidation (HTCO). This involves the flash combustion of a small sample of seawater, typically at 900°C over a platinum catalyst. Although suited for total concentration measurements, the problem of salt formation in the combustion tube makes it rather impractical for larger samples, though it has been used for this purpose with a repeated injection system. The blank reported for a single injection is 11 μM C [5].

Finally, DOC can also be oxidized by oxygen induced by UV irradiation [10]. This method can be operated with large samples and has been used for isotopic ratio measurements.

There has been much confusion about the oxidation efficiencies of the UV, WCO and HTCO methods. Reports have been published claiming that UV and WCO fail to oxidize a substantial part of the DOC contrary to the HTCO method [11–14]. Latter studies have largely reconciled the methods [5]. Most of differences could be traced back to problems with blank subtraction and sample storage problems.

As a new, robust method we present here a supercritical oxidation system which does not suffer from the drawbacks of the other systems mentioned above. The very oxidizing conditions guarantee a complete oxidation. The use of oxygen as oxidator, which is less electronegative than chlorine, prevents the formation of Cl_2. The system is designed for 500–1000 ml seawater samples, resulting in ml CO_2 size samples. This enables the measurement of both carbon isotopic ratios by mass spectrometry techniques, ^{13}C by carbon isotope ratio mass spectrometry, and ^{14}C by accelerator mass spectrometry (AMS). This unique

new combination is an important step in the analysis of the DOC cycle in the ocean which is in turn important in the study of the global carbon cycle. As an example, results obtained for atlantic ocean samples are presented.

2. Experimental

2.1. The oxidation system

The system is shown schematically in Fig. 1. A sample of one liter is placed in a precleaned and flushed bulb, and acidified with 80 μl of concentrated H_2SO_4. The CO_2 present in the sample in the form of dissolved CO_2 gas and HCO_3^- is removed by ''stripping'', i.e. boiling the sample in vacuum for 45 min. Next, $CuCl_2$ is added and the sample is saturated with oxygen by bubbling the solution with a small flow of oxygen during 2 min. The copper chloride is not added earlier to prevent any decomposition during the stripping as this would lead to an unwanted loss of material [5]. During the stripping of CO_2, water evaporates. To correct for the DOC concentration increase caused by the reduction in volume, the sample and the evaporated water (which is trapped cryogenically) are weighed.

An HPLC pump (Gilson 307) equipped with a titanium pump head compresses the sample to 350 bar by setting the pump at a flow rate of 2 ml/min. The high pressure limit of the pump is set to 350 bar. When this maximum is reached, the pump will pause until the pressure drops again below the maximum. This mechanism keeps the pressure in the tube constant within 5 bar. At this pressure the sample is heated to 650°C in an alumina tube with a length of 1 m, an internal diameter of 5 mm and an outer diameter of 8 mm.

The solubility of salts in supercritical water increases with increasing pressure. At the critical point of water 220 bar and 374°C, salts are virtually insoluble, but at our working pressure of 350 bar the solubility is sufficient to dissolve all salts present in seawater, regardless of temperature [15]. This enables the continuous oxidation at high temperatures in the fluid phase. The main experimental problem was the construction of a reactor that can contain the extremely corrosive acid seawater at 340 bar and 650°C. An alumina tube surrounded by a pressurized inconel tube has proven satisfactory [16].

The volume of the hot pressurized water is only 5 ml, limiting the potential danger of the apparatus. Yet some form of shielding of the pressurized system is required for safety. We placed the oxidation reactor in a fumehood and constructed extra shielding with a plate of wood. Shielding is easy, since the high pressure/high temperature part is only connected to the rest of the system by 1/16 in. tubing and electrical wiring.

The water is depressurized to an atmospheric value by leading it through capillary tubing. After some tests, we chose 16 m of 0.18 mm ID PEEK tubing (Upchurch). Tubing with a smaller internal diameter is available (with the advantage of requiring a smaller length), but in our tests it became blocked too often to be of practical use. Even with the present choice of tubing, a 2 μm filter installed after the alumina tube is necessary to prevent blocking.

The oxidized sample is collected in a vacuum glass bulb. After the whole sample has passed the reactor, the CO_2 formed by the oxidation is collected in the usual manner by boiling in vacuum, collecting the water in a dry-ice ethanol trap at −78°C and the CO_2 in a liquid–air cold trap (−193°C). Traces of N_2O, also collected in the liquid–air trap are removed by leading the CO_2 through a 600°C Cu oven.

Sulphur does not give problems as it is oxidized and remains in the water phase. The pressure of the CO_2 in a calibrated volume gives the yield. The original DOC concentration is calculated from the yield and the mass of sample trapped in the glass bulb, corrected for the water frozen in both water traps.

2.2. Reagents

Cuprous chloride and sulfuric acid were obtained from Aldrich with a reported purity of 99.999%. The organic carbon content of these chemicals was not available. The water used in the test was purified by distilling miliQ water over sodium persulfate. Oxygen 5.0 (>99.999% pure) was used for the oxidation reaction.

2.3. Mass spectrometers

The ^{13}C content of the CO_2 was measured on a VG SIRA 9 IRMS. The ^{14}C measurements were

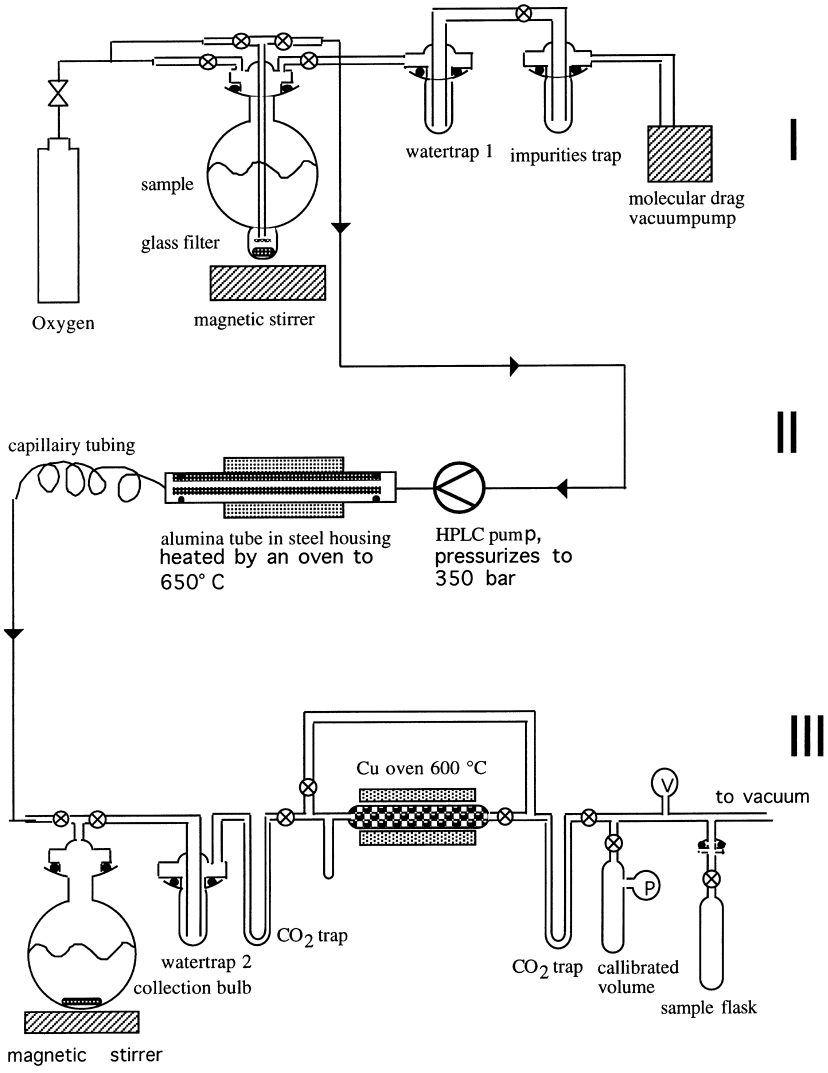

Fig. 1. The supercritical oxidation system, consisting of three sections. The first section (I) is used to remove inorganic carbon and saturate the sample with oxygen. The middle section (II) oxidizes the DOC. Since this occurs in the supercritical state where salts do not precipitate, large samples can be processed without blocking the reactor. The final section (III) isolates and purifies the CO_2 yield. The vacuum part is made of glass; the wetted parts are either glass, teflon, Kalrez, PEEK or stainless steel.

performed with the Groningen accelerator mass spectrometry facility [17]. The sample for this AMS has to be introduced in the form of graphite which is produced by iron catalyzed reduction of the CO_2 by hydrogen [18].

Reported there are the $^{13}C/^{12}C$ ratios expressed as per mil deviations from the international standard (VPDB) [19]:

$$\delta^{13}C \equiv \frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} - 1 \quad (*1000‰)$$

^{14}C activities are reported as percent modern carbon (pmC). This is a linear scale ranging from

0 pmC for material that contains no ^{14}C (such as fossil fuel), to 100 pmC for "modern" natural material [20][1].

3. Results and discussion

3.1. Optimization of the process

There are several variables in the supercritical oxidation method that have to be chosen to optimize its results: pH, temperature, flow rate and choice of oxidator, catalyst and acid. In the following we will discuss our choice of these parameters.

The sample is saturated with oxygen as an oxidator. At room temperature the solubility (in equilibrium with 1.2 bar of oxygen) is approximately 1.6 mM. Typical marine DOC concentrations are in the order of 40 μM, so oxygen is present in excess. The influence of the oxidator in this type of reaction is known to be very limited, both in concentration and type of oxidator [21], so no great surplus or special type of oxidator is required. pH 3 was chosen so that corrosion of the alumina tube was minimal but removal of inorganic CO_2 complete. The flow rate was set at 2 ml/min so that the period at elevated pressure and temperature was long enough to ensure complete oxidation. This limited the throughput to typically one (large size) sample per day. In view of the importance of the data this is acceptable.

Fig. 2 shows the influence of adding copper chloride on the recovery of tannic acid oxidized at 500°C. The temperature was deliberately lowered, so that the oxidation is incomplete, and the catalyst activity could well be observed. Up to 0.5 g the effect is significant, but adding still more gave no further improvement, so 0.5 g was chosen.

Fig. 3 shows the influence of temperature on the recovery of oxidizing phthalic acid (in the presence of 0.5 g $CuCl_2$). At 600°C the oxidation is complete. The working temperature has been set at 650°C to include a safety margin. At higher temperatures the risk of alumina corrosion increases significantly.

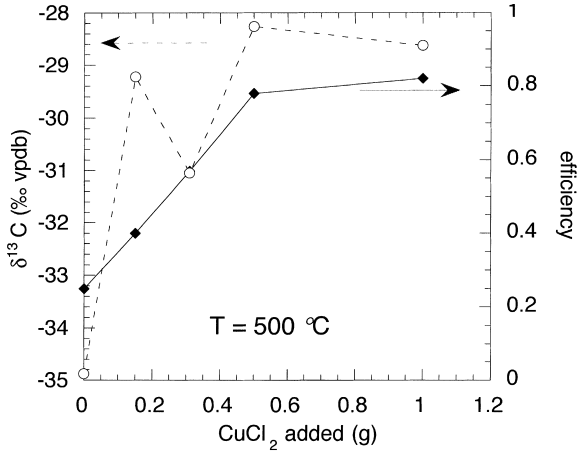

Fig. 2. The influence of the copper concentration on the oxidation efficiency: (◆) and the recovered $\delta^{13}C$; (○) of tannic acid. Copper II ions catalyze the oxidation of organic material under supercritical conditions.

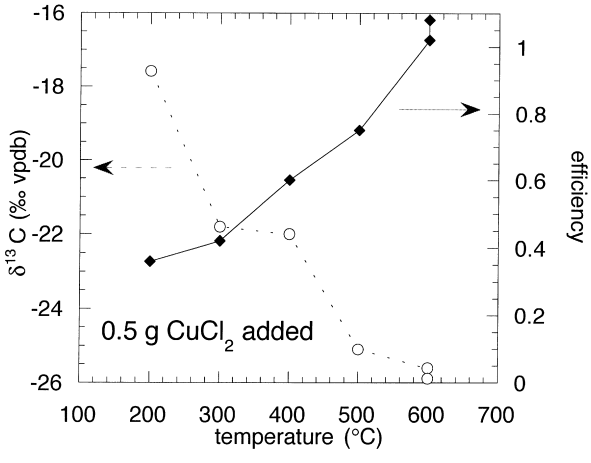

Fig. 3. The influence of temperature on the oxidation efficiency: (◆) and on the recovered $\delta^{13}C$; (○) of phthalic acid in the presence of 0.5 g/l $CuCl_2$.

3.2. Oxidation efficiency

The oxidation efficiency was tested by oxidation of several test substances dissolved in persulfate distilled miliQ water. The results are shown in Table 1. The measured $\delta^{13}C$ values are in good agreement with the

[1]More precisely, a standard material (oxalic acid) has been chosen to be the international reference material, and its $^{14}C/^{12}C$ ratio is defined to be 95 pmC in the year 1950. This value is chosen such that the $^{14}C/^{12}C$ ratio of CO_2 in the natural atmosphere (i.e., before the nuclear bomb tests, and before the dilution of the atmosphere with fossil fuel CO_2) resembles 100 pmC.

Table 1
Test oxidations for $\delta^{13}C$ reproduction and oxidation efficiency

	$\delta^{13}C$ (‰ VPDB)[a]	$\delta^{13}C$ found (‰ VPDB)	Recovery blank corrected
Ascorbic acid	−19.7	−19.5	99
Tannic acid	−26.3	−26.5	101
Thiourea	−23.4	−24.1	94
Urea	−49.7	−48.2	100
Coffeine	−33.1	−33.4	102
Sucrose	−10.4	−11.4	101
Phthalic acid	−25.1	−25.8	99
1-Chloro-2 dimethylamino ethane chloride	−31.6	−26.7	98
Antipyrine	−32.0	−33.4	101
Pyrazine	−23.2	−22.9	97

It shows that for a variety of compounds oxidation is complete and the original $\delta^{13}C$ is reproduced.
[a]VPDB is the international primary reference material with respect to which deviations are expressed in per mille [20]

values measured by direct combustion of these compounds. The accuracy of the resulting $\delta^{13}C$ is also an indication for the completeness of the oxidation. The substances represent several classes of chemicals known to be difficult to oxidize. Urea can resist oxidation by UV light [22] and chlorinated organics are relatively resistant to all oxidation methods. Tannic acid is very refractive in natural environments and therefore a good model for DOC. The thiourea represents the sulfur containing DOC.

Based on the results of the test oxidations, precision in DOC concentration is about 4% of the DOC concentration, precision in $\delta^{13}C$ is about 1‰ and in ^{14}C activity 2 pmC. For very low concentration such as found in deep ocean water, precision will be lower due to variations in the blank. As the measurement of DOC is relative to zero carbon water, accuracy is not defined. The precision of the mas spectrometers (0.5 pmC in ^{14}C content and 0.03‰. in $\delta^{13}C$) is not limiting in this analysis. As in most carbon isotope analyzes, the preparation step from sample CO_2 introduces the major part of the measurement error.

3.3. Blank determination

The blank was determined in two ways: directly by performing the procedure with persulfate distilled miliQ water instead of seawater, and indirectly by calculation from the measured ^{14}C ratios for both a modern (tannic acid) and a synthetic (^{14}C free) model substance (urea). The results are shown in Table 2. Using the fact that the tannic acid had a ^{14}C activity of

Table 2
A summary of blank tests

	$\delta^{13}C$ (‰ VPDB)	$\delta^{13}C$ found (‰ VPDB)	Concentration made (μM C)	Concentration measured	^{14}C measured (pmC)
Blank	—	—	0	7.6	—
Blank	—	—	0	8.0	—
Blank	—	—	0	7.1	—
Tannic acid	−26.3	−26.3	74	80	106
Tannic acid	−26.3	−26.4	69	78	106
Urea	−49.7	−45.6	46	58	19
Urea	−49.7	−44.3	62	72	10

The first three tests show the oxidation of persulfate distilled miliQ water. These show the magnitude or concentration of the blank. The second set of four tests show the results of oxidizing solutions with a known (very low) concentration, and ^{14}C content. From the difference between the original ^{14}C and the recovered ^{14}C, the blank concentration and the blank ^{14}C content can be calculated. This results in a blank of 9 μM with a ^{14}C concentration of 81 pmC.

109% modern carbon, the results in Table 2 result in a total blank of 9 μM C with a ^{14}C content of 80% modern carbon.

Distinguishing between the system blank (carbon coming from the reagents, the tubing, vacuum leakage etc.) and the blank caused by organic material in the water used to determine the blank is difficult. The first source has to be subtracted from the measured values, not the second. This is a problem common to all methods. It is generally agreed upon, that one prepares water with the lowest blank possible, but that one does not attempt to correct for this second contribution in any other way. The total blank estimate of all methods is therefore in fact too high (but by an unknown amount). Still, this blank is subtracted from the measurements.

There is a range of sources for the observed blank. The first danger of contaminations occurs during sample collection and storage. This source is very difficult to tackle; it is not specific for this method. Handling contaminations decrease in general with increasing sample size. As our sample size is much larger than in DOC concentration measurements and we have followed normal procedures in sampling and freezing, we do not expect this to be a problem.

Most important is the complete removal of inorganic carbon. Incomplete CO_2 removal and CO_2 contamination from the oxygen could cause problems. This effect was determined to be 2 μM C in our case, by performing the measurement procedure without applying heat. It is essential that all the inorganic carbon is removed, as this can be present in a concentration 60 times higher than the DOC. At pH 3, assuming an equilibrium of CO_2 between the sample and the vapor above it, the removal of 2 g of water removes 99.999% of the CO_2. With this set-up 10 g of water is removed which is certainly sufficient.

In addition, contamination can be caused by organic material in chemicals, residuals in the vacuum etc. The presence of organic material present in the $CuCl_2$ proved to be negligible because the blank remained constant when the amount of copper chloride was increased tenfold. Increasing the amount of sulfuric acid in the same way as with $CuCl_2$, is not possible because the pH change may increase bleed or corrosion in other parts. Because concentrated H_2SO_4 is used, the added volume is very small. Even if 1% of the acid consists of nonvolatile organic material, an unrealistically high value, the contamination is less than 2 μg of carbon. Vacuum systems are also well-known sources of organic contaminations. This has been prevented by using an oil free molecular drag pump. It is connected to the system via a fluid air cold trap as an extra safety. All remaining contaminations from the vacuum line are thus trapped.

The oxygen used has a quality of 4.8, i.e. 99.995% pure, containing less than 0.5 ppm CH_4 and less than 0.2 ppm CO (The CO_2 present is part of the blank mentioned earlier). The Henry constant of methane in water is 0.035 M/atm. From this constant and the maximum concentration in the oxygen follows that methane cannot contribute more than 1 μg C/l. The valves and pressure regulator are oil free to prevent organics contaminating the oxygen.

After sampling, storage, acidification and inorganic carbon stripping, there is a possible carbon blank contribution from the oxidation system itself. The carbon released by the stainless steel parts has been estimated on the basis of the amount metal ions released. The product contains 0.87 mg/l of iron and 0.72 mg/l of nickel. Together with the nickel and iron, the carbon present in the stainless steel will be released and form part of the carbon blank. Assuming a carbon content of 0.2% in the stainless steel this would give a source of about 1 μg C/l. The only material in the combustion tube is alumina. Traces of alumina, 3 mg/l in the effluent, are released by the tube. No carbon analysis was available for the tubes, but we have sputtered the alumina directly in our AMS and could not detect any carbon. This indicates that it cannot contain serious amounts of carbon. The liquid chromatograph inlet tubing is also a potential source of contamination because it can leach organic material. To minimize this contamination, all wetted parts before the oxidation are made of PTFE, glass or stainless steel.

The variety of potential contamination sources discussed here show the caution required for reliable measurements of DOC from ocean water. There is no single major blank source left (rather multiple minor sources), so it is difficult to further reduce the blank.

3.4. Results on marine samples

Up to now, the system has been used for the analysis of about 40 marine samples, from the world's oceans

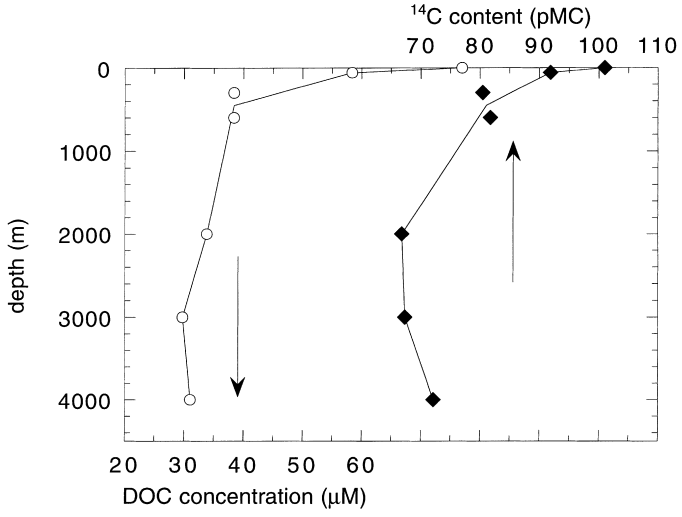

Fig. 4. DOC concentrations: (○, lower scale) and ^{14}C content; (◆, upper scale) as function of depth, from samples in the bermuda atlantic time station (BATS), located in the Western part of the sargasso sea.

and the north sea. Of these 40, about half appeared to be heavily contaminated with enriched ^{14}C material, as it is used for biological labeling studies. In spite of the safety measures on the research vessels, this is apparently a major problem (due to the fact that the ^{14}C concentration of labeled products is many orders of magnitude above natural). However, the system as such performed satisfactorily, and reliable data on 25 samples (including depth profiles) have been achieved. As an example, Fig. 4 shows the depth profile of the DOC concentration and its ^{14}C content for the bermuda atlantic time station (BATS) in the western sargasso sea (taken August 1996). The profile is according to expectations. In short, the higher concentration of DOC in the surface waters is partly composed of fresh, labile DOC with a ^{14}C content that resembles present day air (≈110 pmC). In the deeper waters only the highly refractory part of the DOC, with a higher age, and thus a lower ^{14}C content, survives.

The data have been presented in [23]. First results on the north sea samples can be found in [24]. All data, together with a global model of DOC cycling and ^{14}C activity, will be published in a forthcoming paper.

4. Conclusions

The oxidation system we developed demonstrates the possibility of using supercritical oxidation in an analytical system, even in the most demanding situations (saline solutions, stable compounds and low concentrations). As a measurement system for the concentration and carbon isotope ratios (both ^{13}C and ^{14}C) of marine dissolved organic carbon, it is especially useful as it provides an independent comparison to the more usual methods. In a forthcoming paper, we will apply this method to ocean samples to determine the dynamics of the ocean DOC pool. Continuous measurements of DOC can in principle be performed with an adapted version of this system.

Acknowledgements

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